

trial I found that at the temperature of liquid air n was between 800 and 1000 times as great as at 15° C. With ebonite on the other hand the difference was only about 1.5 to 1.

Preparations are being made for a further series of experiments by a method which will record viscous resistance as well as the amplitude and period of the oscillation.

An Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of very long Vacuum Tubes.

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[PLATES 1 AND 2.]

The spectrum of hydrogen has probably received more experimental study than that of any other element, and yet in spite of the extended series of lines exhibited by solar hydrogen (a Balmer series of 32 lines), the vacuum tube has steadfastly refused to exhibit more than the first 12 members. The solution of the problem looked rather hopeless at the start, for every possible method of electrical excitation, combined with variable gas pressure, various tube diameters, presence or absence of foreign gases and vapours has been tried over and over again. It will be remembered that by employing absorption as a method of locating the lines, I was able to extend the Balmer series of sodium from the eight members previously known in the emission spectrum, almost indefinitely; 48 in the first investigation, and 56 in a subsequent one made in collaboration with R. Fortrat with the very powerful quartz spectrograph of Prof. Weiss at Zurich,* a further extension being merely a matter of increased resolving power and length of the vapour column. This method is impracticable, however, in the case of hydrogen, since this element shows absorption only when subjected to electrical excitation, which of course introduces the same difficulties which occur in the case of the study of the emission spectrum.

The first thing to determine, in attempting to add more lines to a series, is the factor which has heretofore fixed the limit of the series.

A somewhat careful study of the literature on the subject failed to yield any very definite information regarding this matter. I could not, in fact, find any reproduction of a spectrogram of the series which showed more than

* 'Astrophys. Journal,' 1915.

the first five or six lines, and could thus form no idea of the conditions at the portion where the higher members failed to record themselves.

We have, of course, Bohr's theory that the higher members are absent in vacuum tubes owing to the fact that the molecules are too close together to allow room for the very large orbits necessary to give birth to them.

This at all events suggests a method of attack: work at very low pressures and employ very long end-on tubes to give the necessary amount of light. In the case of the end-on capillary tubes as commonly employed, it is doubtful if much light from the remoter parts of the tube reaches the spectroscope. To have every element of length contribute an equal amount of light (neglecting possible absorption by the luminous gas) the following conditions must be fulfilled. The bore must be large enough to permit of the propagation of light according to the laws of geometrical optics, in other words we should be able to see a luminous object distinctly through the tube. The tube should be placed at a considerable distance from the slit of the spectroscope, so that its two ends subtend substantially the same angle as seen from the slit. The aperture of the lens which projects the image on the slit should be restricted to a diameter such that it passes equal quantities of light from the two ends of the tube. This last condition perhaps is not very important owing to internal reflections in the tube, without which the light from the further end of a very long tube will issue in the form of a very narrow pencil of rays, whereas the light from the near end will fill a large cone.

My first tube had a length of about 1.5 metres and was placed at a distance of 3 metres from the spectroscope. Its bore was about 5 mm., and was bent at a right angle near each electrode bulb, the angle of the bend being blown out into a bulb of very thin glass. Clear vision was possible through the tube. To make sure that it was accurately aimed along the axis of the collimator the following expedient was used. A small tungsten lamp with a concentrated filament (motor lamp) was mounted in front of the centre of the collimating lens and the slit opened $\frac{1}{2}$ mm. The diameter of the beam, passed out by the slit, at a distance of 3 metres was about 5 mm. and the tube was mounted in such a position that the rays passed directly down it, the strongly illuminated slit being visible when the eye was brought up close to the bulb.

Though the original plan of working at very low pressures proved to be the wrong line of attack, at least under the present conditions, the experiment led to the discovery of a most remarkable type of tube and a wholly new set of spectroscopic vacuum-tube phenomena. It is probable that a quite new field is opened up for the separation and study of compound spectra. It appeared very early in the experimental work that the obstacle to the

extension of the Balmer series was the faint continuous spectrum, and to a lesser degree the secondary spectrum. In an ordinary vacuum tube the 12th line is so faint that one must know exactly where to look for it, in order to locate it among the numerous lines of the secondary spectrum. Prolonged exposure brings out no new lines on account of the continuous background, which is stronger than the lines sought. Reducing the pressure only makes matters worse, for the intensity of the continuous background increases enormously as soon as the Crookes' dark space exceeds 12 or 15 mm. in thickness. The decrease in the intensity of the lines of the series, combined with the inevitable presence of a continuous background, is evidently what has placed the limit heretofore.

By means of methods to be presently described the series has been photographed down to the 20th line, the intensity of which is probably less than one-millionth that of H_{α} with an exposure of only half an hour in the third order spectrum. True the series has been increased by only eight lines, but when we consider that the 20th line has an intensity of about $1/250$ of that of the 12th line (the previous limit) the advance is seen to be no small one. It has been accomplished by devising a method of practically abolishing the secondary spectrum and the continuous background, or to be more exact, of reducing it to about $1/40$ of the intensity (relative to the Balmer lines) which it has in an ordinary tube.

The discovery of the new type of vacuum tube resulted from the observation that the central portion of the long tube previously described, when viewed through a direct vision prism, showed only the Balmer lines with no trace of the secondary spectrum. The form of tube finally adopted is shown in fig. 1. Its length is about 2 metres, and the bore 7 mm.

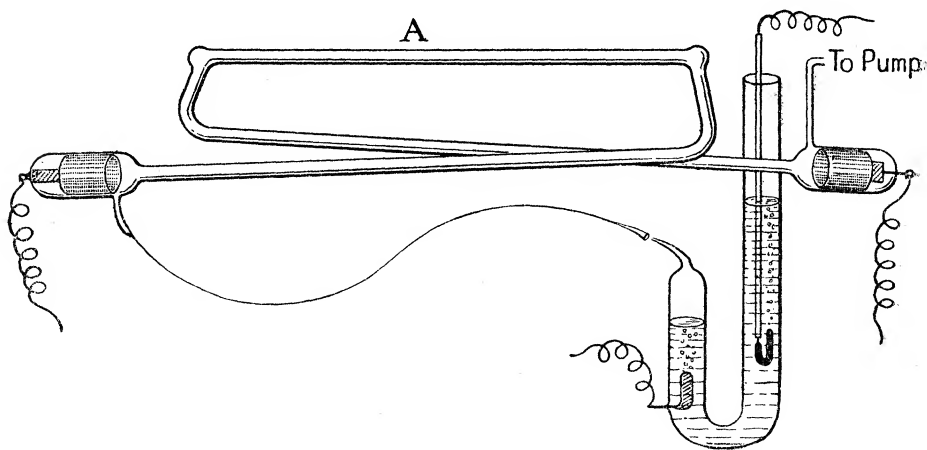


FIG. 1.

The straight portion A is used end-on, and all of the phenomena described in this paper occur only in this portion of the tube, unless specific reference is made to the curved branches. The precise form of the tube is immaterial: it is bent as figured merely to take up less room. The essential thing is to have an end-on portion about 40 cm. in length, separated from each electrode bulb by at least 80 cm. of tubing. One end of the tube is in permanent connection with a Gaede pump, which is usually in continuous operation, while hydrogen is fed continuously into the other end, either moist, from an electrolytic generator, through a long and very fine capillary tube, or dry, through a palladium tube heated in a small flame of hydrogen. The electrodes are cylinders of sheet aluminium, about the thickness of writing paper, and completely fill the glass cylindrical end-bulbs. This type of electrode, being supported by the glass walls, can be very easily inserted, as the sealing-in wire does not have to support the weight of the electrode. The copper plated alloy wire used in lamp manufacture answers admirably.

The tube is operated by the current from a small transformer, giving a potential of about 25,000 volts. Its primary is fed with a 60 cycle A.C., as much as 30 ampères being used on some occasions. Currents as large as 0.2 of an ampère can be carried by the tube with safety, if the hydrogen is at the right pressure.

The appearance of the tube is most remarkable, the colour of the discharge being bluish white to a distance of perhaps 50 cm. from each bulb, while the straight central portion is of a fiery purple, of an intensity which is almost painful to the eyes. If we view the tube through a prism (preferably a large direct vision one) we find that the central portion shows only the Balmer lines, of which four are in the visible spectrum.

The region between the lines is quite black in appearance, and I shall speak of the tube in this condition as in the "black stage." A photograph of a portion of the tube taken through a prism is reproduced, fig. 1, Plate 2.

Viewed through a green colour screen, which cuts off completely the light of the Balmer lines, the tube appears illuminated with a feeble light, which shows that there is a trace of the secondary spectrum left. I have never quite succeeded in abolishing it entirely, though I have, on occasions reduced it to such an extraordinary feebleness, that I have a notion that if the pressure, current intensity and rate of flow of the gas, together with the amount of water vapour present were in very exact adjustment, the secondary spectrum might vanish altogether. The lateral branches of the tube show the secondary spectrum in addition to the Balmer lines, and it is not until we get to a distance of about 50 cm. from the electrode bulbs that it begins to vanish. It will be a matter of considerable interest to investigate

the electrical conditions within the tube, for I imagine that the potential gradient will show marked variations.

This "fractionation" of the compound spectrum into different parts of the tube constitutes one of the many new phenomena exhibited by these very long vacuum tubes, and it is this separation which has made possible an extension of the Balmer series. I shall describe later on how it is possible to abolish completely the Balmer lines and have only the secondary spectrum in the central part of the tube.

It requires some practice in developing the technique of operating the tube before the secondary spectrum can be reduced to the point at which it is no longer visible with the direct vision prism. I have never reduced its intensity to zero, but have obtained a measured intensity of about 1/40 of that shown in the lateral branches of the tube.

The direct vision prism is in constant use during the operation of the tube, and it is well to have in addition a dark green ray filter, absolutely opaque to the light of H_α , H_β , and H_γ .

Through this screen we see the tube only by the light of the secondary spectrum, and can form a better estimate of how nearly we have abolished it. The size and length of the capillary must be so chosen that, with the pump in operation, the depth of the Crookes' dark space is about 6 mm. It is well to have the cylindrical electrodes joined to the sealing-in wire by a narrow strip of aluminium, as shown in fig. 1, for the observation of the dark space, as it cannot be seen to advantage within the electrodes.

The electrolytic hydrogen generator is of the form shown in fig. 1, the electrolyte being a solution of phosphorus pentoxide. It can be left in permanent connection with the battery, as the circuit is automatically broken as soon as the tube is filled with hydrogen. The upper end of the tube is drawn out into a capillary of sufficiently small bore to prevent any considerable escape of the gas during the process of changing the long capillary thread which conveys the gas to the discharge tube. This thread terminates in a short section of tubing with a bore of 2 mm. which is slipped over the generator capillary and sealed with sealing-wax. The other end is then inserted into the discharge tube and sealed in the same way. For the experiments with pure dry hydrogen, I substituted an old X-ray bulb provided with a palladium tube, for the electrolytic generator. The end of the metal tube is heated with a very minute hydrogen flame burning at the tip of a glass capillary.

In constructing the tube care should be taken to avoid having any portion in close proximity with any other portion, as if this is the case the tube is sure to be punctured, owing to the potential difference between the adjacent surfaces.

We will now take up the subject of the extension of the Balmer series, and later on a discussion of some very remarkable spectroscopic phenomena exhibited by this type of tube.

Extension of the Balmer Series.

With the tube in the best condition to which I have been able to bring it, 20 lines of the series have recorded themselves on the plate. Unless the pressure is exactly right, it is difficult to get anything below the 16th. This pressure is such as to give a Crookes' dark space of about 6 mm. If the pressure is gradually raised, the higher members disappear in succession, as they should on Bohr's theory. If the pressure is lowered, they also disappear, though in this case their disappearance seems to be due to a development of a continuous spectrum and the enhancement of the secondary spectrum. There is no doubt whatever regarding the identity of the lines as far down as the 16th member of the series. The identity of the lower members was established by comparison of the plate with one made under conditions giving a strong secondary spectrum and a weak Balmer series. It is possible to bring the tube to what I call the black stage (very weak secondary spectrum) and still fail to secure the higher members. This occurs with a dark space of about 2 mm. The series from the 10th to the 20th member is shown with the iron comparison spectrum by fig. 1, Plate 1, and the series from the 7th to the 14th with the iron spectrum in coincidence by fig. 2. These were taken in the third order spectrum of a large plane grating with a Cook portrait objective of about 1 metre focus. Fig. 3, Plate 1, reproduced as a positive, was made for intensity comparisons and shows the series from the 5th to the 14th line. The strong lines show ghosts, and the oxygen line near H_5 as well as the cyanogen band appear.

Hydrogen.	Wood.	Dyson. (Solar hydrogen.)
12	3722·12	3722·05
13	3712·22	3712·12
14	3703·92	3704·0
15	3697·35	3697·29
16	3691·72	3691·70
17	3686·99	3687·0
18	3682·96	3682·90
19	3679·46	3679·50
20	3676·44	3676·54

The wave-lengths of the higher members are given in the previous table, with Dyson's values for solar hydrogen for comparison. No attempt was

made to get them of a very high degree of accuracy, and they are computed with reference to Rowland's standards of iron, as Dyson's were presumably referred to that scale. Next year they will be more accurately determined with a spectrograph of 20-foot focus, possibly to the fifth order spectrum. These values are certainly correct to 0.1, and possibly to 0.05 of an Ångström.

Impurity Lines.

The following impurity lines have been noticed and identified :—

On the short λ side of H_5 Oxygen 3947.

On the short λ side of H_6 Cyanogen band.

On the short λ side of H_7 Oxygen triplet 3830–3825, *never found*.

On the short λ side of H_{10} Oxygen 3749.5.

On one plate three lines between H_{11} and H_{12} one probably Oxygen 3737.5.

On long λ side of H_{13} Oxygen 3712.9.

On long λ side of H_{14} (*very close*) Hg. 3704.

On long λ side of H_{16} Oxygen 3692.

Other lines are secondary spectrum or mercury.

The study of these lines with the tube in different conditions (pink stage, white stage, secondary flash, etc.) is valuable in formulating a theory of the phenomena.

The Intensity Decrement of the Balmer Series.

Comparison of a number of spectrograms taken with widely different times of exposure showed that in the region between the 6th line and the 14th line each line was very nearly twice as bright as its neighbour on the short wave-length side. To test this a little more exactly, a record was then made of ten exposures in coincidence, each exposure being one-half that of its predecessor—15 minutes, 8 minutes, etc., down to 1.7 seconds. If the law of half intensity held, the lines would be of equal intensities in the diagonal rows, one of which is indicated by a black line on fig. 3, Plate 1. This was found to be the case, as nearly as could be judged by simple inspection of the plate. This means that the 14th line has an intensity of $1/256$ of that of the 6th line. At the same rate of decrease, the value for the 20th line will be $1/15,000$. It seems, however, that the rate of decrease becomes less, the last three lines before the 20th being of not very different intensity.

Between the 6th line and H_a the rate of change is greater (about 2.3), the 6th line having an intensity of, roughly, $1/60$ that of H_a . Calling the 20th line $1/10,000$ of the intensity of the 6th, we find that it has an intensity of something like $1/600,000$ that of H_a . Notwithstanding this, it can be photographed with the long end-on tube in the third order spectrum in

30 minutes without any difficulty. Merton's value of the 4th line for hydrogen and water vapour ($1/100$ of H_α) would give an even lower value for intensity of the 20th line (about $1/4,000,000$ of H_α). Under the present conditions, however, the rate of decrease between H_β and the 6th line was found to be about 2.3. In the case of the nebulae the decrement appears to be much less, the intensity of the 14th line being 2, while that of the 2nd line is only 100.*

Spectrum Phenomena of the Long Tube.

1. *Transfer of Energy from the Secondary to Primary Spectrum.*—Mention has already been made of the fact that only the Balmer series appears in the middle of the tube when the proper condition of the tube is established. A new tube has to be operated for some time before this happens. At first there is considerable secondary spectrum, but it gradually grows weaker, and finally becomes invisible, except when the green screen is employed. This condition I have called the "black" stage. It occurs only with a fairly heavy current. If we put a lamp bank in circuit with the primary of the transformer and turn on one lamp, a very faint discharge occurs, and the secondary spectrum is as strong as, or stronger than, the Balmer series, even in the centre of the tube. If, now, we add another lamp, both spectra brighten, but presently we shall find that the addition of a new lamp (*i.e.*, increase of current in the tube) causes the Balmer lines to *increase* in intensity and the secondary spectrum to *decrease*. If we look at the tube through the green screen, it becomes much darker when the current is increased, a somewhat surprising effect: a lamp which becomes darker when more current is thrown into it! Of course, what really happens is that the Balmer series becomes brighter each time the secondary spectrum is decreased in intensity by the increase of current.

After a certain stage is reached, further increase of current brightens the Balmer lines, but no further reduction of intensity occurs in the secondary spectrum, which remains at a minimum value, or brightens slightly with each enormous increment of intensity of the Balmer lines.

I am of the opinion that it may eventually be possible, by a very precise adjustment of the condition, to reduce the secondary spectrum to zero intensity. If this can be done, photography of the complete Balmer series will be a question only of resolving power and duration of exposure. Experiments along these lines are in progress. The cause of this transfer of energy from one spectrum to the other will be discussed presently, after we have examined some of the other effects observed.

2. *Secondary-spectrum "Flash."*—This is an extremely interesting and

* 'Lick Obs. Report,' 1920.

curious phenomenon. If we bring the tube to the stage at which the secondary spectrum has its minimum value, by gradually increasing the current, and then open the primary switch, we find that, if we view the central portion of the tube through the green screen and close the switch, there is a bright flash which lasts for perhaps $1/10$ of a second, followed by a steady glow of much diminished intensity, which is the permanent minimum value. This can be repeated as rapidly as we can open and close the switch. If we do this very rapidly, the tube is much brighter than if the switch is kept permanently closed, *i.e.*, the integrated intensities of the light of the discharge produced by *short intermittent currents*, is actually greater than the continuous intensity produced by a *steady current of the same value*. (The current is alternating in both cases, of course.) This is true only for the light of the secondary spectrum, and the phenomenon does not occur if the pressure of the hydrogen is too high. The Crookes' dark space should be 4 mm. or 5 mm. in depth. The phenomenon is best seen when moist hydrogen is delivered to the tube directly through the fine capillary. The hydrogen probably is far from saturated with water vapour, however, after traversing the fine tube. With dry hydrogen, obtained with a palladium tube, the phenomenon is absent after all water vapour has been driven out of the glass by long operation of the tube.

The Balmer lines appear to be of low intensity at the moment when the switch is closed, but rise to their full intensity while the secondary flash is subsiding. This phenomenon is less easy to observe, as an initial dim stage of very brief duration, followed by a bright steady state, is less conspicuous to the eye than an initial bright flash followed by a dim stage. The effect was best seen with a rotating mirror and red glass screen. The first three or four discharges of the 60 cycle A.C. were less bright than those following. The recovery of the condition necessary to produce the flash is very rapid, perhaps $1/4$ of a second. A very short interruption of the current (say, $1/20$ sec.) does not, however, renew the flash, the tube remaining dim after the interruption. This effect can be studied by including in the primary circuit a U-shaped strip of metal, and a wire which presses against the inside of the U. By striking the wire over to the other side with the fingers, a very short break can be effected.

The water-vapour band comes out very strongly in photographs taken with the quartz spectrograph (fig. 4, Plate 2). It appears to be relatively stronger with a continuous current than with the short intermittent exposures. This was judged from two spectrograms, one built up by 300 short "flashes" and the other with the switch closed throughout the exposure, the total time of operation of the current being about the same in each case.

The "flash" phenomenon was also looked for in the water band, by means of a screen of barium-platino-cyanide in the focal plane of the quartz spectrograph. It was found to behave in the same way as the Balmer lines, that is, it did not flash bright on closing the switch and then fade away, as does the secondary spectrum.

3. "*Infected*" *Spots on Tube Wall*.—It will be found that certain portions of the tube, far removed from the electrode bulbs, sometimes show the secondary spectrum at the full intensity which it has at the ends of the tube. These spots often form at the sharp angles of the tube. When once formed, they are quite persistent. I have called them "infected" spots, as the phenomenon is evidently associated in some way with the condition of the inner wall of the tube, probably the presence or absence of some adsorbed material. They are sometimes very difficult to get rid of, persisting for days; though I find that by allowing air to enter the tube, and re-exhausting, they frequently disappear entirely. Heating the tube almost to the softening point appears to be without influence either in causing or abolishing these spots. There seems to be another type of infected spot which shows the D lines of sodium. These always appear if the tube is heated to a high temperature. Sometimes a spot only 2 or 3 cm. in length will appear in the straight portion of the tube which shows the yellow light. With the direct vision prism we can at once recognise such a spot, as we see a sharply defined yellow image of the tube in the more or less hazy secondary spectrum. If the discharge is stopped and the tube allowed to cool off, the appearance is normal on renewing the discharge, but the yellow spot develops in a few minutes in exactly the same place. Frequently, pink and white spots alternate along a considerable portion of the tube, the secondary spectrum being weak in the former and strong in the latter. The reverse holds for the Balmer lines.

The appearance is similar to what I have frequently observed in Claude's neon lamps, which were to be generally observed in Paris during the winter before the war, glass tubes 20 or 30 feet long, containing neon and mercury. Small portions of the tube often exhibited only the mercury spectrum, though the greater part glowed with the brilliant orange red of neon. I believe that these tubes were furnished with mercury electrodes, and the local patches of blue colour are evidently regions where the mercury vapour is in excess of the neon. These spots often moved about in a curious manner, fading away and then appearing at another point. There may be something of the same kind going on in the hydrogen tube, though I do not feel certain that the cases are analogous. Certain spots in the tube sometimes show almost no trace of the Balmer lines. H_{α} faint and

H_{β} barely discernible. At these spots the secondary spectrum has great brilliancy. Close to the electrode bulbs, where the discharge is strongly stratified, the Balmer lines fade away rapidly. No trace of H_{α} or H_{β} can be seen in the first stratum, H_{α} is barely visible in the second, and both can usually be seen in the third or fourth. It will be remembered that Fulcher found that the low potential discharge (hot cathode) in hydrogen showed the secondary spectrum very strong and the Balmer lines weak.

4. *Change of Spectrum after Prolonged Operation.*—We have already discussed the remarkable change which occurs in perhaps 1/10 second, which has been termed the "secondary flash." There is another change, which occurs with a heavy current, after an operation of perhaps half a minute. At the start we have the "black stage," *i.e.*, no secondary spectrum visible, between H_{α} and H_{β} . In about 15 seconds a trace of the secondary spectrum appears, and it becomes quite marked after a minute's operation. If, now, the switch is opened, and the tube allowed to rest for two or three minutes, the black stage is found again on closing the switch. This is the *reverse* of the flash phenomenon, and the recovery is slow, whereas, in the case of the flash, the recovery is very rapid. It is my opinion that the rapid recovery of the flash condition is connected with a change occurring in the whole mass of the gas in the tube, whereas the other phenomenon, with the slow recovery, is associated in some way with adsorption of ionised hydrogen or water vapour by the wall of the tube. Langmuir* found that the ionised (atomic) hydrogen given off from a tungsten filament was powerfully adsorbed by the wall of the tube, but that, on heating the wall, it was liberated as molecular hydrogen.

5. *Suppression of the Balmer Series. The White Stage.*—The effects described in the four preceding sections are observed with hydrogen containing water vapour. Passing the hydrogen over, phosphorus pentoxide did not appear to have much influence on the general appearance of the tube, though the "secondary flash" was not as conspicuous as before.

On substituting a palladium tube for the electrolytic generator, no very marked effect occurred on the first day, but, towards the end of the second day, after the tube had been in operation for almost ten hours, a sudden change occurred. During the two days' work, the tube had repeatedly been exhausted and recharged with hydrogen from the palladium tube. Between the tube and the pump was a trap immersed in liquid air, to prevent the diffusion of mercury vapour and vapour from the stop-cock grease, since

* Langmuir, "The Dissociation of Hydrogen into Atoms," 'Journ. Amer. Chem. Soc.,' August, 1914.

there appeared to be some reason to suspect that these vapours were influencing the results.

Numerous spectrograms were taken during the two days, without anything peculiar being noted, except the gradual disappearance of the great water band, when suddenly a very remarkable thing happened. On closing the switch, the central portion of the tube was fiery purple as usual, with little or no secondary spectrum; in about ten seconds it became a whitish pink, and presently bluish white, the direct vision prism showing that practically all of the light now came from the secondary spectrum. After the current had been passing for about two minutes, however, the pink colour returned, the secondary spectrum faded away, and the Balmer series rose again to its usual brilliancy. The electrical current was now stopped, the pump put in operation and the tube exhausted until the bulbs showed green fluorescence on momentarily closing the switch. (If the switch is closed for more than a few seconds with the tube in this stage the bulbs are invariably either punctured, as by a spark, or a small spot is fused and blown in by atmospheric pressure, the bulb appearing as if pushed through with a needle.)

Fresh hydrogen was now admitted as usual, by heating the palladium tube in a minute hydrogen flame for 30 seconds. This time, however, the white stage did *not* appear. After a number of exhaustions and refillings it suddenly came again, and I found, after a number of trials, that while, as a rule, the purple colour is present on closing the switch, if the discharge is stopped as soon as the white stage is at its best (*i.e.*, Balmer lines at minimum intensity) and the tube re-exhausted and then refilled with fresh hydrogen, *the white stage always appears the moment the switch is closed*. If, however, the discharge is continued until the purple stage sets in, and is then stopped, on exhausting and re-charging the tube, the *purple* stage always appears on closing the switch and persists for 5 or 10 seconds, gradually passing over into the white stage, and then again into the purple stage. I have sometimes succeeded in getting the tube into such a condition that the white stage persisted indefinitely with continued operation.

The white stage is produced at its best only after being repeatedly produced. It may require an hour or two of work. Then H_{β} is practically invisible in the direct vision prism, and there is only a faint trace of H_{α} . The fading away of H_{β} is an interesting phenomenon to watch. It usually weakens first at the ends of the straight central portion of the tube, the weakening pushing in towards the centre from the ends, until finally the line fades away entirely. This is the moment at which the current must be stopped, and the tube re-exhausted and re-filled, to get the best condition for the appearance

of the white stage on closing the switch. I did not succeed in completely abolishing H_{α} , though I put the tube through this cycle of operations for an entire day. Possibly, if it were persisted in for a longer time, H_{α} would finally go. Apparently, the production of the Balmer series requires a trace of water vapour. The long operation of the tube, with repeated exhaustions and re-chargings with dry hydrogen, finally removes the water occluded by the glass, and we then get the secondary spectrum only.

Continued operation at the white stage may eventually liberate more water vapour from the glass, and the purple stage then reappears. The difficult question is: "Why do we have the purple stage on closing the switch, followed in a few seconds by the white stage?" The clue to the answer is evidently to be found by considering the peculiar difference in the initial condition (at the closing of the switch) *according to whether we stop the discharge (and re-fill the tube) at the white stage or at the purple stage.* Since what we introduce into the tube is the same in each case, the difference must be in the condition in which we leave the wall of the tube. If the Balmer lines (which give the pink colour) depend upon the presence of water vapour we must conclude that the vapour is liberated from the surface of the glass the moment the current is started. This gives the pink stage. To account for the white stage which immediately follows, we must assume that the water vapour disappears; just how this happens is not easy to say. It may be dissociated and the ions driven away from this portion of the tube, but the fact that the Balmer lines fade away first at the *ends* of the straight central portion of the tube seems to be against this view. The subsequent re-appearance of the purple stage can be explained by the heating of tube by the prolonged operation, more water being driven to the inner surface and liberated. If we stop the discharge at the white stage (in which condition the inner *surface* of the tube is free from water), and allow the tube to cool off, exhaust and re-fill, we get the white stage at once on closing the switch, as the inner surface of the tube is still free from water.

Difficulty is sometimes found in bringing the tube to the white stage. That we are approaching the condition is indicated by the appearance of the green and yellow mercury lines half a minute or so after closing the switch. The best plan to follow is to operate the tube for several hours on the heaviest current which it will bear, say 2 ampères, exhausting and re-charging every ten minutes or so. The current must be stopped as soon as the discharge shows signs of "flickering" in the bulbs (which occurs just before the cathode ray fluorescence appears), otherwise the bulbs will be punctured. Then reduce the current to 0.05 ampère and stop the discharge each time at the moment when the secondary spectrum attains its maximum

intensity which will occur in half a minute or so after closing the switch. Then exhaust and re-charge, repeating the above-described operation. Each time it will usually be found that the Hg lines and the secondary spectrum will become stronger, and presently the white stage will appear. It requires some patience to coax the tube into this condition, but the phenomenon is very striking when it finally occurs.

Spectra showing the gradual transition from the time of first starting the tube to the white stage are reproduced on fig. 4, Plate 2. H_{β} is the line at the extreme right, and the lower spectrum was taken first, with the tube containing some air (nitrogen bands show). The ammonia lines also appear on this plate.

The transitions from the pink to the white stage, and back were studied with a small quartz spectrograph, which required an exposure of but a few seconds and was well adapted to catch the transient stages of short duration. On looking over these plates I found that all spectra of the white stage showed, in addition to the secondary spectrum, a pair of lines between H_3 and H_4 . I have indicated them by two arrows on fig. 3, Plate 2. The lower spectrum shows scarcely a trace of them; this was made when the white stage was less perfectly developed, H_2 being still visible to the eye. On photographs made of the secondary spectrum under ordinary conditions (hydrogen with a trace of water vapour and small current) there is absolutely no trace of them. On another occasion, when the tube had a very minute leak, sufficient only to give a dark space of 3 mm. after standing highly exhausted over night, I found that when the white stage developed, the spectrum showed chiefly the nitrogen bands. A similar phenomenon was found with helium. On closing the switch the line spectrum was all that could be seen, and the tube was bright yellow; but after a minute or two, a brilliant white patch developed, which showed the nitrogen bands.

When the tube had been brought to a point very near the "white stage" and the Balmer lines were comparatively weak, a small amount of oxygen was admitted to the tube, and photographs made every five seconds with the quartz spectrograph. The addition of the oxygen caused the Balmer lines to brighten and the secondary spectrum to diminish in intensity. No trace of the water band was visible in the first exposure, but it appeared after one minute's operation of the tube. The tube was then highly exhausted and fresh hydrogen admitted through the palladium tube. The Balmer lines were bright and the secondary spectrum very weak; there was no trace of the water band during the first five seconds but it developed after a run of one minute. These experiments make it appear as if the water vapour was adsorbed by the wall as rapidly as it formed, and was then liberated again as

the temperature of the tube rose. This is a matter, however, which requires further investigation. The appearance or no appearance of the oxygen line near hydrogen line No. 5 should be noted in this connection.

These points will be investigated in the near future.

6. *Spectra of Stratifications.*—At pressures at which the tube is usually operated, stratifications appear only in the vicinity of the electrode bulbs. In some cases, when the discharge passed into the white stage described in the previous section, stratifications suddenly filled the entire bulb, though no change had been made in the pressure or potential.

It is possible to have the stratifications appear in the secondary spectrum and not in the Balmer lines: this condition is best obtained by blowing a small bulb in the straight central part of the tube. The bulb acts as a sort of secondary electrode and stratifications develop on both sides of it. Under certain conditions of pressure and potential it was found that (when the tube was viewed through the prism) the secondary spectrum showed the stratifications while the Balmer lines did not. This seems to establish, beyond any doubt, that the spectra are emitted by different entities, for which other evidence exists. A photograph made of the tube and bulb when in this condition, made with the direct vision prism, is produced on fig. 2, Plate 2. It shows strong stratifications in the secondary spectrum, no trace of them in H_α or H_β , a faint trace in H_γ , and increasing traces as we pass to higher members of the series. This apparently proves that the lines of the Balmer series are emitted by different entities, since the discharge may be seen strongly stratified in the 5th line, while no trace of the strata appears in the 1st.

These facts were very carefully studied visually, the intensity of H_α and H_β being reduced by neutral grey absorbing films, but no trace of the strata was found, though the higher members showed them clearly in the photographs. Faint traces of stratification may be easily lost in a photograph through over-exposure. Another photograph, made on an isochromatic plate, which was very insensitive to H_α , showed well the complete absence of any trace of discontinuity.

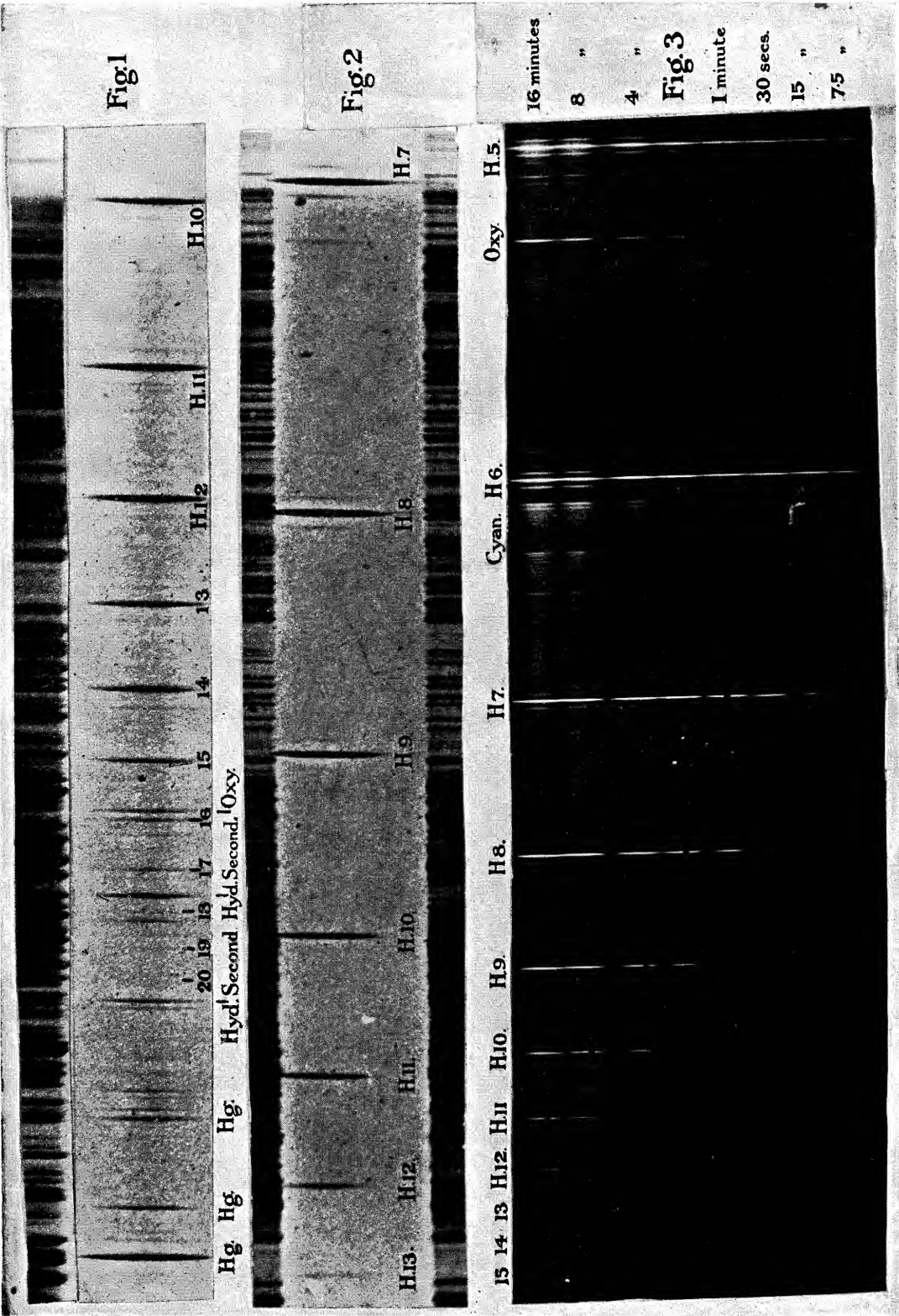
The strata near the electrode bulbs are sharply defined. They all radiate the secondary spectrum strongly, but no trace of the Balmer lines appears in the first stratum which emits the secondary spectrum alone, a trace of H_α appears in the second stratum, H_α and H_β appear in the third, while further along the series appears in considerable intensity. No difference in the *spacing* of the strata for the two spectra has been observed, which appears to be of importance.

It is also worthy of remark that very often when the tube passes from

the pink to the white stage, the entire bulb suddenly fills with stratifications, though no change in the current or the pressure has occurred.

A general discussion of the results recorded in this paper will be more profitable after further investigations have been made. In the autumn I plan to immerse the central portion of the tube in liquid air, which I expect may give the white stage at once. It is also of importance to identify the two lines which appear when the white stage sets in, between the 3rd and 4th hydrogen lines. I made an effort to do this during the last few days before closing my laboratory for the summer, employing the grating instead of the quartz spectrograph, but the tube developed a microscopic leak, and when the white stage finally appeared it showed only the nitrogen bands.

It appears to be well established that pure dry hydrogen gives only the secondary spectrum at any great intensity, and that, for the strong development of the Balmer lines, a trace of water vapour is required. It was found that the same thing could be accomplished with oxygen. Experiments have also been made with helium and with oxygen in the long tube, but the results are still incomplete. In the case of oxygen a curious phenomenon was observed at one stage of pressure, the colour of the discharge changing suddenly, and the soft glass tube phosphorescing with a ruby-red light. I suspect that this red phosphorescence is due to extremely short wave-lengths, which suddenly develop.



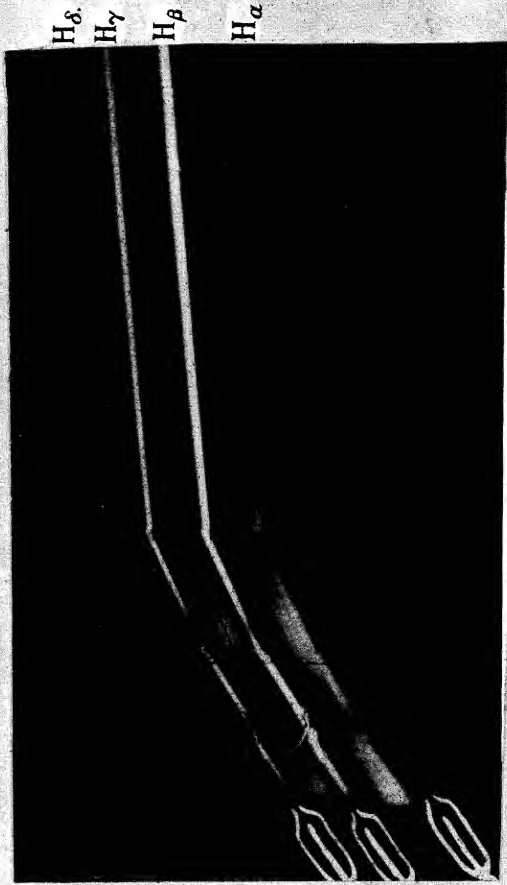


Fig1

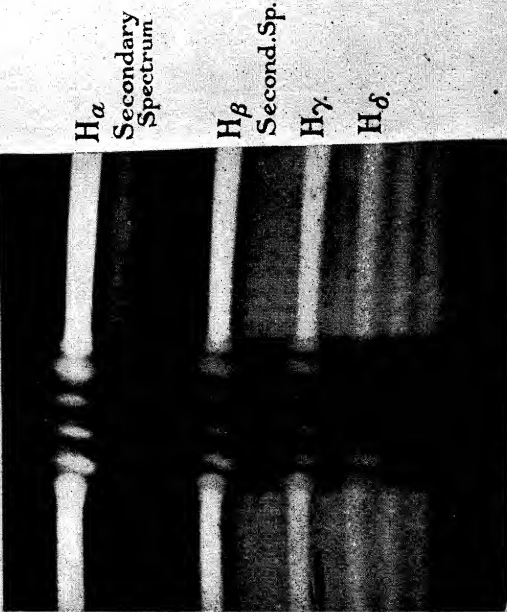


Fig2

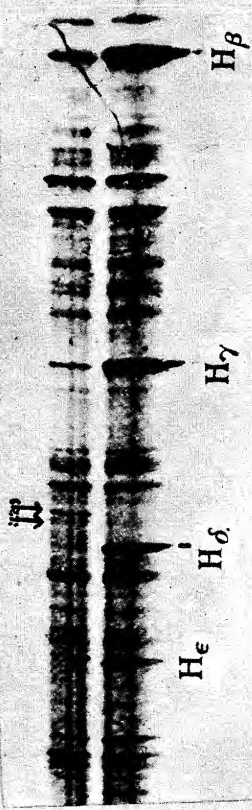


Fig3

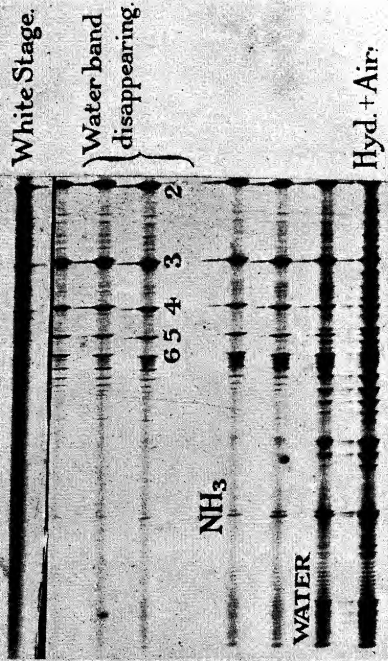


Fig4

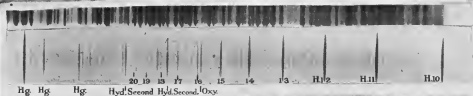


Fig. 1

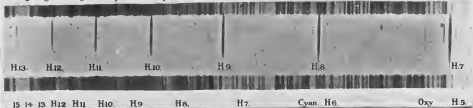


Fig. 2



Fig. 3

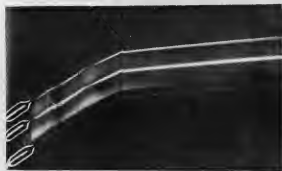


Fig1



Fig2

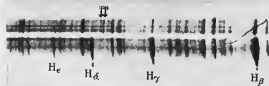


Fig3

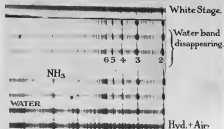


Fig4